The Chilean Nitrate Deposits

George E. Ericksen

The origin of the Chilean nitrate deposits, which contain a unique group of saline minerals, has provoked lively discussion for more than 100 years

The nitrate deposits in the extremely arid Atacama Desert of northern Chile are among the most unusual of all mineral deposits. In fact, they are so extraordinary that, were it not for their existence, geologists could easily conclude that such deposits could not form in nature. The nitrate deposits consist of water-soluble saline minerals that occur as cement in unconsolidated surficial material (Fig. 1)—alluvial fill in valleys, loose rock debris on hillsides, and windblown silt and sand—and as impregnations and veins in porous and fractured bedrock. They are found chiefly along the eastern side of the Coastal Range, but also within the Coastal Range, in the Central Valley to the east, and along the lower Andean front (Fig. 2). Features of the deposits that appear to defy rational explanation are their restricted distribution in a desert characterized throughout by saline soil and salt-encrusted playas; the wide variety of topography where they occur; the abundance of nitrate minerals, which are scarce in other saline complexes; and the presence of other, less abundant minerals containing the ions of perchlorate, iodate, chromate, and dichromate, which do not exist in any other saline complexes. Iodate, chromate, and dichromate are known to form under such conditions, but no chemical process acting at temperatures and pressures found at the earth's surface is known to produce perchlorate.

Because of their obscure origin, the nitrate deposits have been the subject of lively discussions for more than 100 years, but none of the dozens of published reports about them gives an adequate or wholly acceptable explanation for the sources of their saline constituents and their modes of emplacement. As I have pointed out (Ericksen 1979, 1981), the most important factor in the accumulation and preservation of the nitrate deposits has been an extremely arid climate in the Atacama Desert, similar to the present nearly rainless conditions, that has persisted since the deposits began to form some 10–15 m.y.a. I believe that the principal sources of most

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of the saline constituents were the volcanic rocks of late Tertiary and Quaternary age in the Andes, and that the nitrate is chiefly of organic origin.

The Chilean nitrate deposits have played an important role in modern agriculture and industry, and the history of their development is a fascinating saga (see Bermudez 1963; Ericksen 1963). They were the chief source of fixed nitrogen for explosives, fertilizer, and a variety of industrial chemicals from the 1830s to the 1930s and were virtually the only source of iodine—previously extracted from seaweed—from the 1870s to the mid-twentieth century, when iodine began to be recovered from oil- and gas-well brines. The first recorded shipment of sodium nitrate from Tarapacá, then the southernmost province of Peru, consisted of about 700 metric tons sent to Europe in 1830. However, the first treatment plants were built near Zapiga between 1810 and 1812, and prior shipments of nitrate to Europe were probably made to establish markets. Small amounts of sodium nitrate were recovered for use in the manufacture of explosives for local mines in the mid-eighteenth century, perhaps as early as the 1720s. Pre-Columbian Indians are thought to have used natural material containing more than 50% sodium nitrate as fertilizer.

After 1830, the nitrate industry grew rapidly in response to the demand for nitrate for fertilizer, and by 1843, annual exports were about 16,000 metric tons. Production continued to increase, although sporadically because of periodic oversupply, and reached a maximum of nearly 3 million metric tons during World War I. It declined temporarily after the war and then again increased, to the all-time high of 3.1 million metric tons of sodium nitrate (equivalent to about 511,000 metric tons of contained nitrogen) in 1928. Production of synthetic nitrogen compounds, first made on a commercial scale at the beginning of World War I, surpassed that of Chilean nitrate in the early 1930s. The Chilean deposits never recovered their former dominance; by 1950, they accounted for only about 15% of the world market for fixed nitrogen, and in 1980 their share was an insignificant 0.14%. The phenomenal growth in the demand for fixed nitrogen compounds since World War II has been due largely to the rapidly expanding use of nitrogen fertilizers. In 1980, global production reached 70.8 million metric tons of contained nitrogen, which is about three times the nitrogen content (23.4 million metric tons) of all the sodium nitrate produced in Peru and Chile since 1830.

Resources of sodium nitrate in commercial-grade Chilean nitrate ore (at least 7% sodium nitrate) are esti-

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Figure 1. The typical alluvial nitrate workings shown here are in a broad, flat-floored valley at the western side of Salar de Bellavista in northern Chile (see Fig. 2). These deposits, which consist of saline-cemented surficial material, apparently formed in and near a playa lake that formerly covered this area. Stagnant saline waters of the former lake and associated ponds and moist soils are believed to have contained abundant microorganisms, which were active in transforming atmospheric nitrogen into the nitrate now found in the minerals of the deposits. Some of the nitrate and other saline materials that accumulated in the playa were carried by wind to the surrounding hills; condensate from the frequent winter fogs stabilized these wind-blown materials, which were then washed into the soil by infrequent rains. (All photos are by the author.)
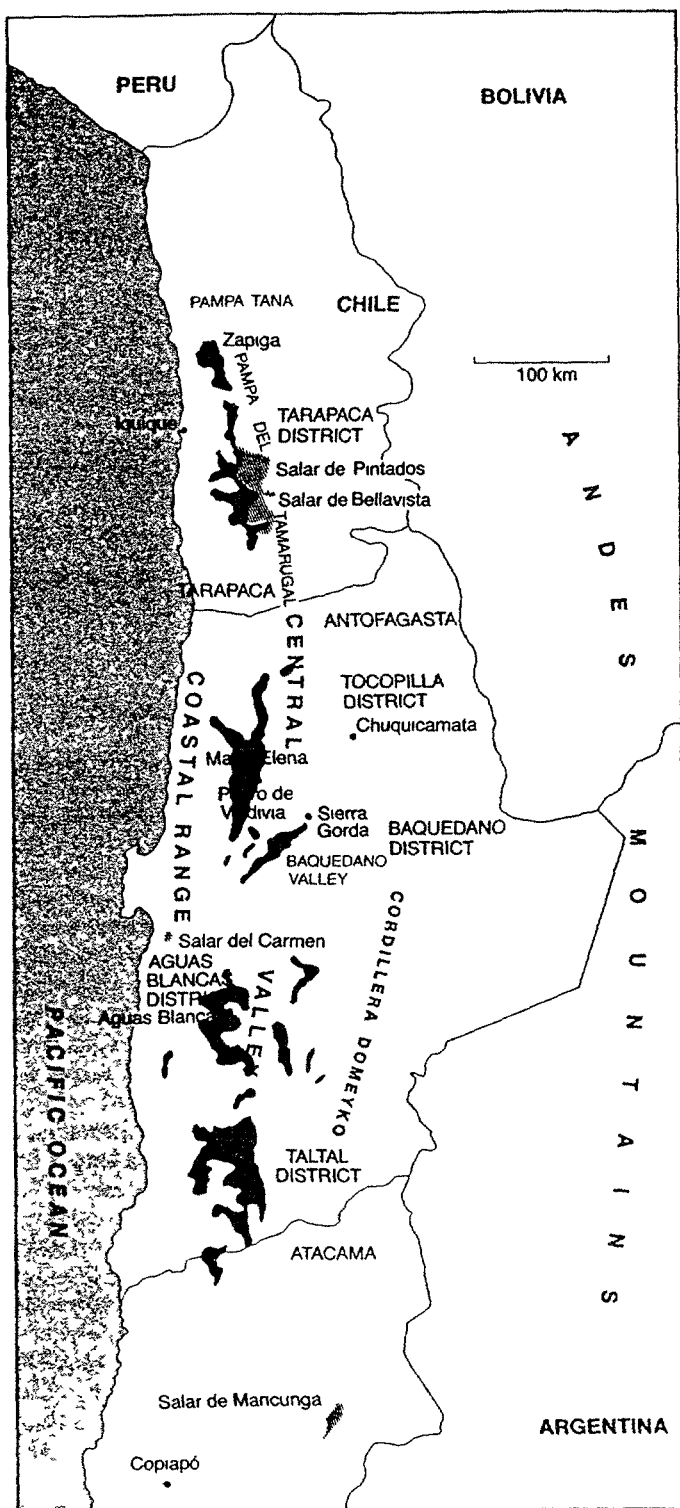
mated to be about 200 million metric tons (Ericksen 1963), equivalent to 32.9 million tons of contained nitrogen, or less than half the world consumption in 1980. There may be several times as much lower-grade material, but that still would not be sufficient to supply world demand for more than a year or two.

Where the deposits occur

The nitrate deposits are in the two northernmost Chilean provinces of Tarapacá and Antofagasta in a band up to about 30 km wide, extending approximately from latitude 19°30′ S to 26° S, a distance of about 700 km. The deposits in Tarapacá and northern Antofagasta are largely restricted to the eastern side of the Coastal Range, but the deposits to the south are spread out more widely in the Central Valley and gentle slopes of the Cordillera Domeyko, one of the ranges of the Andean front. The deposits in the Baquedano district are in a broad, transverse, debris-filled valley draining southwestward into the closed basin of Salar del Carmen. Noncommercial nitrate deposits and nitrate-rich soils are much more widespread than the commercial deposits, evidently forming an almost continuous band throughout the area of the richest deposits. Nitrate is also found in the Pampa Tana, which is along the lower Andean front in southern Tarapacá and northern Antofagasta, and in the vicinity of Salar de Maricunga in the high Andes northeast of Copiapó in northern Atacama Province (see Fig 2). Most of the deposits are at altitudes of 1,000–2,000 m, but those along the western side of the Cordillera Domeyko extend upward to altitudes of about 3,000 m, and those at Salar de Maricunga are near 4,000 m.

The dominant physiographic features of the Atacama Desert are the Coastal Range and the segmented Central Valley, which separates the Coastal Range from the Andes. The Coastal Range, 10–50 km wide, is an area of low relief and subdued topography. Most of the tallest peaks are 1,500–2,000 m high. The Central Valley consists of the broad, nearly flat, alluvium-filled depression called the Pampa del Tamarugal in northern Antofagasta and southern Tarapacá provinces, which is interrupted by the transverse Baquedano Valley extending from Sierra Gorda to Salar del Carmen. To the south the Central Valley appears as a broad basin of interior drainage centering at Aguas Blancas. This depression disappears near the northern limit of the Taltal district, where broad transverse valleys drain directly to the coast.

The Atacama Desert is characterized by abundant saline minerals such as halite, gypsum, and thenardite, which occur as cementing minerals in soils, as impregnations and veins in bedrock, and as saline-encrusted playas. The nitrate deposits are anomalous concentrations of nitrate, iodate, borate, chromate, and perchlorate ions in an otherwise normal desert saline complex. However, saline minerals are much more abundant in the Atacama than they are in most other deserts, and its unusual saline accumulations, in addition to the nitrate deposits, include veins of halite, bloedite, and, more rarely, sodium nitrate, in the oxide ore—the upper part of ore bodies affected by weathering—of metal-bearing deposits. Such veins occur at the famous Chuquicamata copper mine. One of the principal copper minerals in the oxide ore at Chuquicamata and other copper deposits in the Atacama Desert is the oxychloride mineral atacamite.

(Mortimer and Sarič 1972, 1975). As a consequence of this long-term aridity, the present-day landscape, particularly that of the Coastal Range, has been modified only slightly since the middle Miocene, and some landforms may date from the Eocene. In the modern Atacama Desert as a whole, measurable rainfall—1 mm or more of rain—may occur as infrequently as once every 5 to 20 years; in the areas of the nitrate deposits, these rainfalls probably average out to an annual rate of not more than 1-2 mm.

Only a few times each century is there a heavy rainfall of 1 cm or more, which may continue intermittently for several days with an aggregate precipitation of several centimeters. Because rainwater soaks into the ground with little or no runoff, gullying is rare, and some of the large valleys in the Coastal Range lack well-defined stream courses. Infrequent local torrential rains cause flooding and gullying, but the general absence of stream erosion has given rise to the typical smooth or rounded topography in which hills, gullies, and valleys of an early erosion cycle are covered with debris from nearby bedrock, mixed or covered with windblown sand and silt. Sand dunes are absent in most of the Atacama Desert; a single dune field occurs 20-30 km east of Salar de Pintados, and a few large dunes are found along the coast and in the Coastal Range.

Most of the region is devoid of plants, except along courses of streams draining from the Andes and in the Pampa del Tamarugal, where the water table is near the surface. Sparse grass and shrubs grow on hills near the coast, where they can survive on condensate from the common winter fogs. An unusual feature of the Central Valley and some of the closed basins in the Coastal Range of Tarapacá is the presence of abundant groundwater, which in some places is only a few meters below the surface. This groundwater is recharged by stream runoff and by subsurface water flowing from the Andean region, where rainfall averages 100–250 mm per year. Groundwater in the basins in the Coastal Range is resupplied by water flowing below the surface along fault zones connecting these basins with the Pampa del Tamarugal.

A temperature inversion along the coast of northern Chile, due to the Peru-Chile Current, causes frequent winter fogs. The fog forms as a cloud bank several hundred meters thick and generally several hundred meters above the ocean's surface; it sweeps inland nearly every night during the winter months of June to August. The fog commonly blankets much of the Coastal Range, and condensate from it is often sufficient to dampen soil and rock surfaces. This condensate probably plays a role in stabilizing windblown surface salt, initiating movement of the salt down into the soil and fractured bedrock. The salt is then washed to greater depths by the infrequent rains.

The Andes of northern Chile were the site of intense volcanic activity during the late Tertiary and Quaternary periods, and volcanic rocks and thermal

The copper iodide mineral marshite occurs at Chuquicamata and the silver iodide mineral iodargyrite at silver mines in the Atacama Desert; these minerals were formed by reaction between primary copper and silver minerals and iodine in saline solutions in the weathering zone.

The Atacama Desert has had an extremely arid climate, comparable to the nearly rainless climate of the present, at least since the middle Miocene era, 10–15 m.y a., and before that a somewhat less arid climate that may have extended back to the Eocene, about 50 m.y.a

springs have been major sources of saline material in the many Andean salars—the Spanish name for salt-encrusted depressions or playas—and in the salars and soils of the Atacama Desert, including the nitrate deposits. Late Tertiary rocks in this region consist of a thick sequence of silica-rich rhyolitic tuffs, light-colored volcanic rocks having abundant quartz; Chile has one of the greatest accumulations of these types of rocks on the earth. The rocks are capped by hundreds of volcanic cones, chiefly of andesitic rocks, which are darker and contain less silica and somewhat more magnesium and iron than the rhyolitic rocks. Only a few of these volcanoes have erupted during historic times, but several now emit hot gases and vapors. The tuffs contain abundant water-soluble salts, as indicated by salt encrustations along streams and marshes in the Andes, and are clearly the dominant sources of the chloride, sulfate, and borate minerals in Andean salars. They also are the sources of the anomalous lithium in the brines of many of these salars.

Geology and composition

Nitrate deposits are found in all types of topography, from the tops of hills and ridges to the centers of broad valleys and basins. However, many of the richest deposits, which were worked extensively during the nineteenth century, are on the lower slopes of hills, bordering a salt pan or playa like that shown in Figure 3. The deposits occur in all types of rocks and unconsolidated sediments without showing any systematic variation in the relative amounts of the different saline constituents. High-grade nitrate ore is found in such diverse rock types as granitic intrusions, andesite and rhyolite flows and tuffs, limestone, sandstone, and shale. However, the most extensive deposits are those in which the saline minerals form a cement in unconsolidated surficial material. Saline minerals were deposited in pores, cavities, and fractures in the host rock and in new openings formed by the force of crystallization. Features such as compositional layering, desiccation polygons, lesa-cakes, sand dikes and associated veins, and layers of relatively pure humberstonite, thenardite, or gypsum near the surface—all of which are discussed below—are common in all the deposits, and reflect the secondary structures that formed during and after the accumulation and enrichment of the saline constituents (Ericksen 1963, 1981). $Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$

Two types of nitrate ore may be distinguished: alluvial ore, such as that shown in Figure 1, in which the saline minerals act chiefly as a cement in unconsolidated surficial material, and bedrock ore, like that pictured in Figure 3, in which minerals form impregnations, veins, and irregular masses in the bedrock. The alluvial ore generally rests on poorly cemented or uncemented material similar to that in the ore itself, whereas the rock below the bedrock ore is less fractured or more impervious, and relatively free of saline minerals. The typical alluvial nitrate deposit is made up of several layers, as shown in Figure 4. The ore layer, or caliche, is generally 1–3 m thick, but layers as thin as 50 cm and as thick as 5 m have been mined locally. Steeply dipping veins and horizontal or gently inclined layers of high-purity, white, nitrate-rich saline material (called caliche blanco by the miners) are widespread in some alluvial deposits
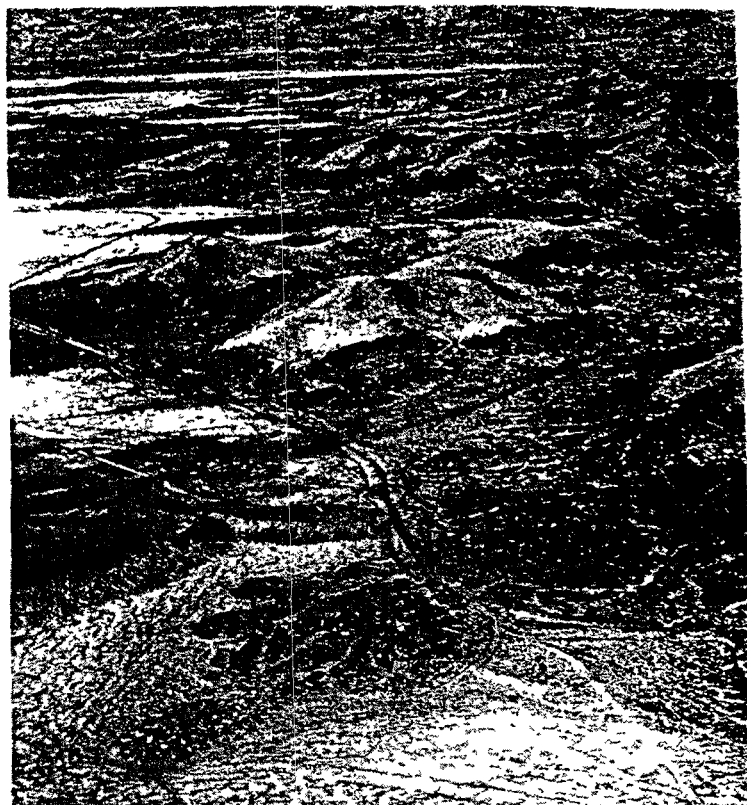

Figure 3. These nitrate workings in the northern part of the Tarapacá district are typical of deposits in bedrock. High-grade nitrate deposits were mined across the tops of low, island-like hills of bedrock in the playa in the foreground, on the lower slopes of the hills in the middle distance, and in the broad, alluvial basins and flats in the background. Waste dumps of treated ore can be seen in the left foreground.

but relatively rare in others. Most such veins and layers are 10–50 cm thick. Near-horizontal layers, if present, are usually at the base of the nitrate ore.

Compositional layering in alluvial ore is the result of leaching of saline minerals near the surface by the infrequent rains, and redeposition of the minerals at deeper soil levels. As a result, the least soluble sulfate minerals tend to be concentrated near the surface and the most soluble nitrate minerals at depth. Halite, the only chloride mineral in these deposits, is abundant in both the costra and the ore layer. The alluvial ore has abrupt horizontal variations in composition that are generally unrelated to the physical character of the host rock. The relative amounts of the dominant chloride, sulfate, and nitrate minerals in a given layer or part of a layer of ore may vary drastically over horizontal distances as small as a few tens of centimeters. High-grade nitrate ore may change to ore not worth mining within a few meters, without any obvious difference in appearance.

In bedrock ore, the veins and layers of caliche blanco occur along fractures in rocks not showing layering, such as rhyolite tuff (Fig. 5), and along fissures parallel to layering and in crosscutting fractures in layered sedimentary rocks. The caliche blanco formed along incipient cracks and narrow fissures that were gradually forced open as the saline minerals crystallized. It generally ranges from a few centimeters to several tens of centimeters in thickness and is usually at a depth of 3–6 m, but at places is as much as 12 m below the surface. In a given bedrock nitrate deposit, the ore tends to be at a relatively constant depth and, like alluvial ore, it tends to be par-
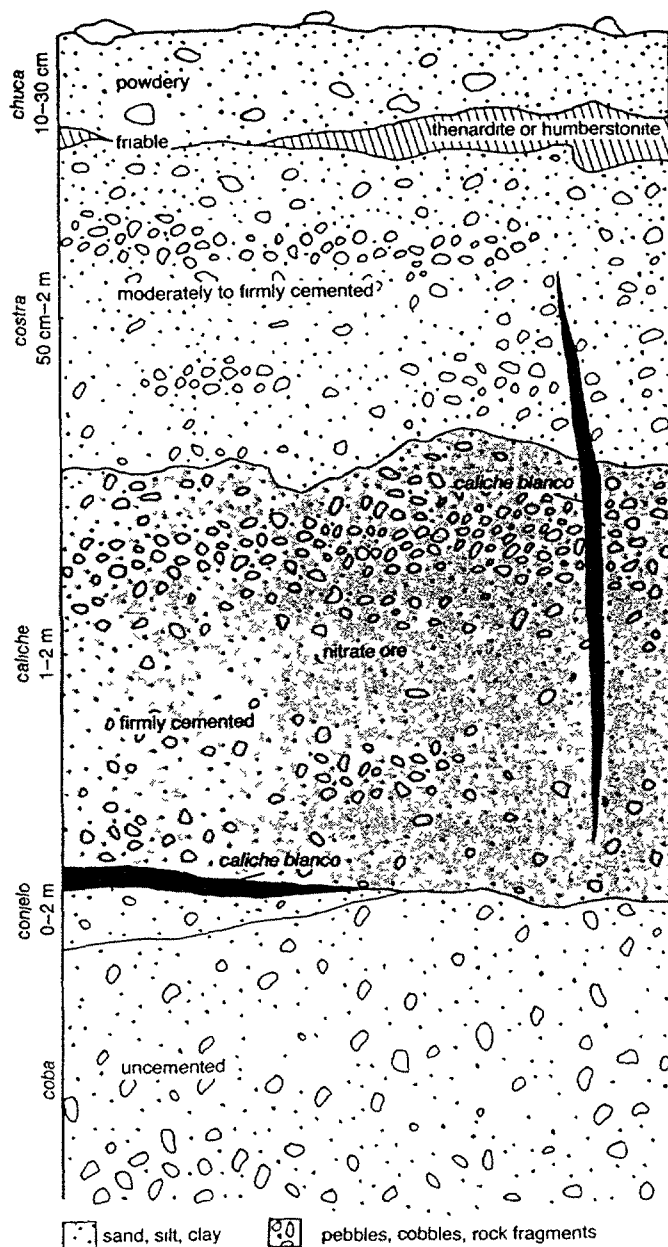
Figure 4. In an alluvial nitrate deposit, the saline minerals occur as a cement in loose, surficial material that covers the bedrock, and as relatively pure local veins and layers, called *caliche blanco*, that filled open fissures in the saline-cemented material. The characteristic layering is due to leaching and redeposition of the saline minerals by water from infrequent rains, which wash down the most soluble substances such as sodium chloride and sodium nitrate. *Chuca* and *costra* are layers over the ore, or *caliche*, that contain little or no nitrate. Fractures and fissures, which cut into both the *costra* and the *caliche*, are cracks developed during desiccation or by tectonic movement. *Conjelo* and *coba* are low-grade or barren material below the ore. (From Ericksen 1981.)

allel or nearly parallel to the surface.

Past and present slow desiccation of the nitrate deposits has resulted in small desiccation polygons (Fig. 6), as well as larger polygons several meters in diameter. After prolonged leaching, the small polygons may be transformed into spheroidal cakes of anhydrite, called *losa*, embedded in a powdery matrix (Fig. 7). Marginal open fissures of the large desiccation polygons become filled with saline-cemented sand, silt, and rock debris a few centimeters to several tens of centimeters thick, called sand dikes (Fig. 8). Most sand dikes are richer in nitrate than the ore around them is; some contain small veins of saline minerals. Analogous to these dikes are the massive veins of *caliche blanco* that formed in open fissures. The saline minerals in the dikes and veins are the result of selective leaching of saline material near the surface and redeposition at deeper levels.

In some places the *chuca* contains layers of relatively pure sulfate minerals—humberstonite, bloedite, gypsum, anhydrite, or thenardite—which formed when the more soluble nitrate and chloride minerals were washed deeper into the soil. These layers are generally soft and powdery, but some, particularly those consisting of humberstonite or bloedite, contain dense, hard, brittle masses that appear to have been deposited as gels. These masses, which blend into the surrounding layer, become powdery as the result of slow recrystallization caused by moisture from fog condensate and rain.

The nitrate deposits are unique in both chemical composition and mineralogy. In addition to a high concentration of nitrate, they have exploitable quantities of iodine; an extremely high ratio of iodine to bromine, which is the reverse of the relative abundances of these two elements in other saline deposits; and the only perchlorate ion known to occur naturally. The iodate, chromate, and dichromate minerals—lautarite, brüggenite, dietzeite, tarapacaite, and lopezite—are known only from these deposits, as is humberstonite, a nitrate mineral. The other nitrate minerals—soda niter, niter, and darapskite—are constituents of the so-called cave nitrates, which formed by decay of bat guano; these minerals are rare or absent in most other accumulations of saline materials, although they do occur in a few small deposits of nitrate-rich saline materials in other deserts that are analogous to the Chilean deposits.

Because of the great local and regional variations in relative amounts of the saline constituents, the chemical composition of an average or typical nitrate ore is difficult to estimate Perhaps the best approximations are those based on large tonnages of ore processed by the nitrate treatment plants. For example, from 1932 to 1967, the two largest plants, María Elena and Pedro de Valdivia, had a combined annual production of about a million metric tons of sodium nitrate. Based on monthly averages for this period, the ore treated by these plants had the following average content of ionic saline constituents: 10.0% sulfate, 6.9% sodium, 6.3% nitrate, 4.6% chloride, 1.8% calcium 0.7% potassium, 0.5% magnesium, 0.5% borate, 0.06% iodate, and 0.03% perchlorate (Grossling and Ericksen 1971).These constituents, which represent the water-soluble material, make up an average of nearly a third of the nitrate ore, with the remainder being insoluble rock debris and saline minerals of low solubility. Higher-grade nitrate ores that were mined selectively during earlier days generally contained two or three times as much nitrate, and during the earliest period much of the mined ore was relatively pure *caliche blanco* that was at least 40% sodium nitrate.

One of the problems of estimating the chemical composition of the nitrate ore is the lack of complete chemical analyses of the saline constituents. The routine analyses by the processing companies show only the

components that are dissolved by hot water, and as a result underreport the components occurring in minerals of low solubility. Among these are calcium and sulfate in the abundant minerals gypsum and anhydrite, iodate in the relatively sparse calcium iodate minerals, and borate, chiefly in the mineral ulexite. Furthermore, sodium, the most abundant metallic ion, is not analyzed—the values cited in the previous paragraph were calculated to maintain stoichiometric balance among the ionic components.

Of the many saline minerals present, halite and soda niter are by far the most abundant, being the dominant minerals in nearly all nitrate ore. Although the total sulfate may equal or exceed nitrate, it is contained in several minerals, each of which alone is rarely more plentiful than soda niter. The most abundant sulfate minerals are bloedite, gypsum, anhydrite, and glauberite. The nitrate-sulfate minerals darapskite and humberstonite also occur in quantity. Thenardite, which is an abundant mineral in other desert saline deposits, is rare in the nitrate ore because it is unstable in the solutions from which sodium nitrate precipitates (Ericksen and Mrose 1970).

Typical nitrate ore is hard and dense, and the saline constituents generally have a fine granular texture. Most of the saline minerals are white and are so intimately mixed in typical ore that it is difficult or impossible to distinguish the distinct mineral species in individual specimens. Cavities in the ore commonly contain small but well-formed crystals, and there are some veins or parts of veins essentially composed of only one mineral, such as the high-purity veins of soda niter shown in Figure 5. During field studies, I have encountered similar veins of halite, glauberite, and bloedite. Crystals of halite, soda niter, darapskite, lautarite, brüggenite, dietzeite, lopezite, thenardite, gypsum, and anhydrite have been found in cavities. Small tufts of fibrous probertite and hydroboracite also appear in cavities, but ulexite generally occurs as fine, needle-like crystals and clusters of crystals embedded in the granular saline matrix

Origin of the deposits

Many theories about the origin of the Chilean nitrate deposits have been proposed or elaborated since Charles Darwin, who visited the deposits in northern Tarapacá in July 1835 during the voyage of the Beagle, speculated that they were formed at the margin of an inland extension of the sea (Darwin 1890) Almost every conceivable source and mode of accumulation for the nitrate has been suggested; most theories either ignore the sources of the other constituents or assume they are compatible with the proposed source of the nitrate.

Among the many sources of nitrate that have been suggested are: decay of seaweed and other marine vegetation in waters and marshes of partially cutoff inland arms of the sea (Forbes 1861; Noellner 1867, Flagg 1874, Muntz 1887) or of vegetation in saline lakes of continental origin (Sieveking 1878); nitrification and leaching of seabird guano (Hillinger 1860; Gautier 1894, Penrose 1910), or accumulation of windblown ammoniacal particulate matter and gas from extensive guano deposits that were presumed to have existed along the coast of northern Chile (Ochsenius 1887–88, Brüggen 1928),

Figure 5. Veins of nearly pure sodium nitrate occur in fractures in rhyolite tuff, a volcanic rock that is widespread in the central part of the Taltal district. A chemical analysis of a sample of material from one of these veins shows that it is 99% sodium nitrate, the richest *caliche blanco* reported from northern Chile.
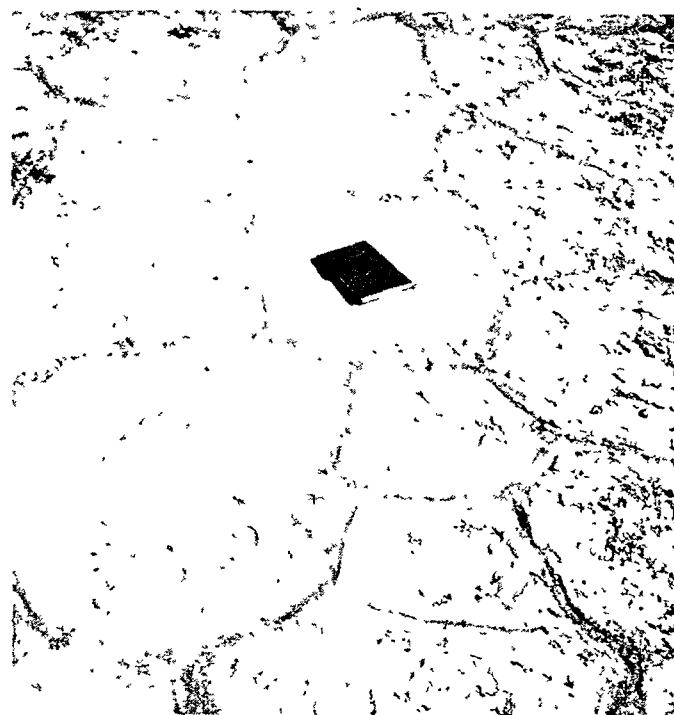

Figure 6. Small desiccation polygons are clearly visible in *costra* that has been swept free of *chuca*. Cracks at the margins of the polygons contain saline-cemented sand and are analogous to the sand dike shown in Figure 8. Small polygons such as these are usually confined to the *costra*, generally extending to depths of not more than 50-75 cm; larger polygons, which may be several meters in diameter, have marginal cracks and fissures that commonly extend to the bottom of the nitrate ore. The sand dike shown in Figure 8 occupies such a fissure.

bacterial decay of plant and animal remains during the Tertiary and Quaternary periods when a less arid climate supported abundant vegetation in northern Chile (Plagemann 1897–98), or decay of ancient plant material in soils (Newton 1896); nitrification and fixation of atmospheric nitrogen by bacteria in the soil (Gale 1912; Brüggen 1938); reaction of atmospheric nitric acid with feldspathic igneous rocks of the nitrate fields (Pissis 1878, Sundt 1904; Wetzel 1928; Knoche 1930); accumulation of nitrogen compounds of volcanic origin in gases associated with intense volcanism in the Andes (de Kalb 1916, Fiestas 1922, Steinmann 1925) and in nitrate-rich salts leached either from volcanic rocks of Jurassic age (Whitehead 1920) or from rhyolitic ash-flow tuffs of late Tertiary and Quaternary age (Ericksen 1961); and accumulation of nitrate from diverse sources in the subsurface saline waters and brines of salars (Singewald and Miller 1916; Mueller 1960) or in the soils of the nitrate fields (Claridge and Campbell 1968; Ericksen 1979).

According to these theories, the saline constituents of the deposits accumulated by: evaporation of saline waters at the margins of inland arms of the sea or saline lakes, or within such bodies of water or marshes that subsequently evaporated completely; capillary migration of subsurface saline water and brine from salars into soils and fractured rock of nearby hillsides, where the saline materials were deposited by capillary evaporation; fallout or precipitation from the atmosphere, and reactions of atmospheric constituents with soils; and accumulation as flows of saline-rich mud on hillsides in the nitrate fields after heavy rains. Wetzel (1924) has been the only adherent of this last proposed mode of accumulation.

Figure 7 Cakes of the mineral anhydrite, called *losa*, are embedded in the powdery *chuca* of this nitrate field in the northern part of the Tarapacá district These cakes are believed to have been formed by prolonged leaching by fog condensate, dew, and infrequent rain in a terrain marked by small desiccation polygons like those shown in Figure 6.

None of these theories gives a wholly adequate explanation of the origin of the nitrate deposits. My proposal (Ericksen 1979, 1981) of a model for atmospheric transport and deposition of the saline constituents from diverse sources explains the great vertical range of the deposits—from hilltops to valley bottoms—but does not explain the limited areal distribution of the richest deposits. On the other hand, alternate proposed modes of transport and deposition—groundwater, saline lakes, and mud flows—alone cannot explain either the vertical or the areal distribution. The origin is neither simple nor obvious.

An acceptable explanation of the deposits' origin must take into account the sources and modes of accumulation of saline materials in the present-day Atacama Desert. These include accumulation and evaporation of saline water in salars and playa lakes, and atmospheric fallout of wind-transported material. Capillary evaporation of groundwater in salars and playas is an important method of salt deposition, but no evidence points to any significant capillary migration of groundwater outward and upward from salars or playas, an effect that has been called on to explain the areal distribution of the deposits. The chief sources of saline constituents in the modern Atacama Desert are volcanic rocks and emissions in the Andes, and spray from the nearby Pacific Ocean, chiefly in the form of evaporated particulate saline material.

The origin of the Chilean nitrate deposits remains speculative, and present-day investigators continue to have divergent views about the sources of the saline constituents and their modes of accumulation. As new data have become available over the years, my ideas about the origin of the deposits have undergone many changes The widespread saline materials in the Atacama Desert probably come from diverse sources and were transported to the sites of deposition by wind and water In 1981, I suggested that the spacial relation between salars and playas and the nitrate deposits indicated a genetic relation, and that transport by the wind of particulate saline material and spray from lakes in the playas probably accounted for significant amounts of saline material in the nearby nitrate deposits. In that report I also suggested that nitrogen compounds in ocean spray and others formed by photochemical and electrochemical reactions in the atmosphere were the chief sources of the nitrate I now believe that these were the sources of only a small portion of the nitrate and that most of it formed by fixation of atmospheric nitrogen by microorganisms in playa lakes and associated moist soils (Ericksen, unpubl.).

The most likely events in the formation of the nitrate deposits are as follows: Most of the commercial nitrate deposits shown in Figure 2 accumulated during times when the runoff from slightly greater than usual rainfall in the Andes resulted in widespread playa lakes in the Atacama Desert. Thick and extensive playa sediments in the Central Valley of northern Chile indicate that such periods of increased rainfall were numerous during late Tertiary and Quaternary periods, the last 10–15 million years Nitrate deposits formed in and near these lakes by direct crystallization of saline minerals in the lakes when they periodically evaporated to dryness and as efflorescences on moist soils above near-surface

Figure 8. This nitrate-rich sand dike formed when loose material from the surficial layer of *chuca*, windblown silt and sand, and material sloughed from the fissure walls filled a fissure caused by desiccation in an alluvial nitrate deposit. This loose filling was then firmly cemented by saline minerals deposited by rainwater. Dikes such as this one are commonly richer in nitrate than the surrounding ore because of the leaching and redeposition caused by the rainwater.

groundwater. Wind subsequently spread part of these saline accumulations out to form deposits in nearby hilly terrain.

Ever since their formation, the deposits have undergone changes due to leaching and redeposition of the saline constituents by rainwater. This is a kind of secondary enrichment that accounts for the layering of the alluvial deposits and the abundance of exceptionally high-quality deposits on the lower slopes of hills.

The chief sources of the ordinary saline constituents—sulfate, chloride, sodium, calcium, magnesium, and potassium—are water-soluble saline minerals in the volcanic rocks of the Andes, which are leached by rainwater and carried into the desert chiefly by streams and groundwater, and wind-transported particulate salts of evaporated spray from the Pacific Ocean. Widespread borate in the nitrate deposits and trace amounts of lithium are clearly of volcanic origin.

The sources of the more exotic constituents—nitrate, iodate, perchlorate, and chromate—are less well understood. I believe that most of the nitrate was formed by nitrogen fixation and nitrification of ammonium by blue-green algae and bacteria in playa lakes and nearby moist soils; photochemical processes in the atmosphere and at soil level in the nitrate fields may have produced additional nitrate. For instance, some nitrate may have been formed by photochemical oxidation of ammonium

in sea spray, as suggested by Bloch and Luecke (1972) based on their discovery that spray has a relatively high concentration of ammonium (100 ppm in spray versus 0.1 ppm in seawater) However, it is unlikely that oceanic ammonium was a major source of nitrate in the deposits because salt encrustations on hills near the seacoast include much sea salt but relatively little nitrate (a sample I collected from a hill several kilometers east of Iquique contains 84.8% sodium chloride and only 0.19% nitrate).

The most likely sources of iodine are iodine-rich organic films on the sea surface (see MacIntyre 1974), which are ejected in spray or from which the iodine evaporates as a gas, and gases and sublimates associated with Andean volcanism, part of which would be carried into the nitrate region in groundwater and surface water. In both cases, the iodine would later be oxidized to iodate, probably by photochemical reactions in the atmosphere or at ground level in the nitrate fields. Bromine is at least an order of magnitude more abundant than iodine in nearly all inorganic materials, including the ocean and the thermal springs associated with volcanism in the northern Chilean Andes, whereas it occurs only as traces—less than 0 01%—in the nitrate deposits. Inasmuch as iodine and bromine have similar chemical and physical properties, it would be expected that they become concentrated in the nitrate deposits in propor-

tions similar to those of the source material. The greater abundance of iodine suggests either a source enriched in iodine relative to bromine, such as organic films on the sea surface, concentration of iodine by the microorganisms in the playa lakes associated with the nitrate deposits, or photochemical oxidation to the relatively stable iodate, perhaps on soil surfaces in the nitrate fields, with bromine either not oxidized and escaping as gaseous bromine and bromic acid, or oxidized to gaseous bromous oxide. I believe one of the first two explanations is most likely.

Perchlorate may have been formed by photochemical reactions, perhaps between chlorine and ozone in the atmosphere or at ground level. Simonaitis and Heicklen (1975) theorized that perchloric acid could be formed by such reactions in the stratosphere; similar reactions might take place in the troposphere.

The source of chromate is especially mysterious because chromium-rich rocks are absent in northern Chile, and water-soluble chromium salts are not known to be associated with volcanic rocks. However, since the amount of chromium in ocean water is insignificant, one is led to the conclusion that the chromate was leached from large volumes of rock, chiefly the late Tertiary and Quaternary volcanic rocks of the Andes, and slowly concentrated in lakes and ponds of the Atacama Desert. The more rare dichromate is an altered form of chromate, as can be deduced from its association with chromate minerals in the nitrate deposits.

Studies related to the extraction of nitrate from the complex ore of the Chilean deposits, principally during the latter part of the nineteenth century and early part of the twentieth, have contributed significantly to the development of industrial chemistry. Geological investigations have supplied new information about the physical and chemical character of the deposits, potential sources of their saline constituents and their modes of accumulation, and the nature of the environment in which the deposits formed. These findings give us a better understanding of desert saline complexes as a whole and of the processes involved in their formation.

References

Bermúdez M., O. 1963. Historia del salitre desde sus orígenes hasta la Guerra del Pacífico. Santiago: Ediciones de la Universidad de Chile.

Bloch, M. R., and W. Luecke. 1972. Geochemistry of ocean water bubble spray. *J. Geophys. Res.* 77:5100–05.

Brüggen, J. 1928. La geología de los yacimientos del salitre de Chile y las teorías que tratan de explicar su origen. *Sociedad Nacional de Minería, Boletín Minero* 40:394–406.

———. 1938. El salitre. *Sociedad Nacional de Minería, Boletín Minero* 50:737–54.

Claridge, G. G. C., and I. B. Campbell. 1968. Origin of nitrate deposits. *Nature* 217:428–30.

Darwin, C. 1890. *Journal of Researches into the Natural History and Geology of the Countries Visited during the Voyage around the World of H.M.S. 'Beagle.'* New ed. Appleton.

de Kalb, C. 1916. Origin of nitrate. *Mining and Scient. Press* 112:663–64.

Ericksen, G. E. 1961. Rhyolite tuff, a source of the salts of northern Chile. In USGS professional paper 424-C, pp. C224–25.

———. 1963. Geology of the salt deposits and the salt industry of northern Chile. USGS Open File Series, no. 689.

———. 1979. Origin of the nitrate deposits of northern Chile. In *Actas*

of the Congreso Geológico Chileno, 2d, Arica, vol. 2, pp. C181–205. Santiago: Instituto de Investigaciones Geológicas.

———. 1981. Geology and origin of the Chilean nitrate deposits. USGS professional paper 1188.

———. Unpubl. Meditations on the origin of the Chilean nitrate deposits.

Ericksen, G. E., and M. E. Mrose. 1970. Mineralogical studies of the nitrate deposits of Chile. II, Darapskite, $Na_3(NO_3)(SO_4) \cdot H_2O$. *Am. Mineral.* 55:1500–17.

Fiestas, B. 1922. El origen del salitre. *Caliche* 4:97–106, 145–53.

Flagg, J. W. 1874. Nitrate of soda, its locality, mode of occurrence and methods of extraction. *Am. Chemist* 4:403–08.

Forbes, D. 1861. On the geology of Bolivia and southern Peru. *Geolog. Soc. of London Quarterly J.* 17:7–62.

Gale, H. S. 1912. Nitrate deposits. USGS Bull. 523.

Gautier, A. 1894. Sur un gisement de phosphates de chaux et d'alumine contenant des espèces rares ou nouvelles et sur la genèse des phosphates et nitres naturels. *Annales des Mines*, sér. 9, 5:5–53.

Grossling, B. F., and G. E. Ericksen. 1971. Computer studies of the composition of Chilean nitrate ores: Data reduction, basic statistics, and correlation analysis. USGS Open File Series, no. 1519.

Hillinger, J. C. 1860. Cited in J. T. Singewald, Jr., and B. L. Miller, 1916, The genesis of the Chilean nitrate deposits, *Econ. Geol.* 11:103–14.

Knoche, W. 1930. Zur Entstehung des Chile-Salpeters. *Forschungen und Fortschritte* 6:196–97.

MacIntyre, F. 1974. Chemical fractionation and sea-surface microlayer processes. In *The Sea*, vol. 5, *Marine Chemistry*, ed. E. D. Goldberg, pp. 245–99. Wiley.

Mortimer, C., and N. Sarič R. 1972. Landform evolution in the coastal region of Tarapacá Province, Chile. *Revue de Géomorphologie Dynamique* 21:162–70.

———. 1975. Cenozoic studies in northernmost Chile. *Geologische Rundschau* 64:395–420.

Mueller, G. 1960. The theory of formation of north Chilean nitrate deposits through "capillary concentration." In *Report of the Twenty-First Session*, pt. 1, pp. 76–86. Copenhagen: International Geological Congress.

Müntz, C. A. 1887. Origen de los depósitos del nitrato de soda. *Sociedad Nacional de Minería, Boletín* 4:719–20, 727–28.

Newton, W. 1896. The origin of nitrate in Chili [sic]. *Geolog. Mag.*, new ser., decade 4, 3:339–42.

Noellner, C. N. 1867. Über die Entstehung der Salpeter- und Boraxlager in Peru. *Journal für praktische Chemie* 102:459–64.

Ochsenius, C. 1887–88. La formación del nitrato sódico de sales de aguas madres. *Sociedad Nacional de Minería, Boletín* 4:752–53, 757–60, 765–67, 5:776–78, 781–82, 789–90.

Penrose, R. A. F., Jr. 1910. The nitrate deposits of Chile. *J. Geol.* 18:1–32.

Pissis, A. 1878. Report upon the Desert of Atacama, its geology and mineral products. In *Nitrate and Guano Deposits in the Desert of Atacama*, pp. 1–30. London: Taylor and Francis.

Plagemann, A. 1897–98. Sobre la formación geológica del salitre bajo el punto de vista de la fermentación química. *Sociedad Nacional de Minería, Boletín* 9:88–93, 153–56, 245–48, 323–26, 409–12, 583–89, 10:12–15.

Sieveking, J. P. 1878. Chilean nitre-beds. In *Nitrate and Guano Deposits in the Desert of Atacama*, pp. 38–43. London: Taylor and Francis.

Simonaitis, R., and J. Heicklen. 1975. Perchloric acid—A possible sink for stratospheric chlorine. *Planetary and Space Sci.* 23:1567–69.

Singewald, J. T., Jr., and B. L. Miller. 1916. The genesis of the Chilean nitrate deposits. *Econ. Geol.* 11:103–14.

Steinmann, G. 1925. Über den Chemismus in der Wüste. *Naturhistorischer Verein der Preussischen Rheinlande und Westfalens Sitzungsberichte* 1924A:8–12.

Sundt, L. 1904. Los ajentes atmosféricos i su obra en el desierto de Atacama. *Sociedad Nacional de Minería, Boletín* 16:17–33.

Wetzel, M. 1924. Petrographische Untersuchungen an chilenischen Salpetergesteinen. *Zeitschrift für praktische Geologie* 32:113–20, 132–42.

———. 1928. Die salzbildungen der chilenischen Wüste. *Chemie der Erde* 3:375–436.

Whitehead, W. L. 1920. The Chilean nitrate deposits. *Econ. Geol.* 15:187–224.